

STABLE ISOTOPES IN ALH84001: AN ION MICROPROBE STUDY. J. M. Eiler¹, J.W. Valley², and. E.M. Stolper¹, ¹Geological and Planetary Sciences, Caltech, Pasadena, CA 91125, eiler@expet.gps.caltech.edu, ²Geology and Geophysics, University of Wisconsin, Madison, WI 53713

The temperature of formation of carbonates in ALH84001 provide a test of the hypothesis that they contain features produced by ancient martian life [1], and contributes to our understanding of the global budgets of martian volatiles. We have determined the μm -scale distribution of O and C isotope ratios in carbonate concretions, enstatite and SiO_2 in ALH 84001 by ion microprobe as a means of constraining the range of possible temperatures of fluid-rock interaction [2]. Principal results are: (1) carbonate $\delta^{18}\text{O}$ is 9.5–20.6‰, SMOW, significantly expanding the range from bulk analysis. The magnesite rim is higher in $\delta^{18}\text{O}$ than Ca-rich ($0.07 \leq X_{\text{Ca}} \leq 0.13$) cores. (2) Variations in $\delta^{18}\text{O}$ occur over length scales as small as 50 μm . (3) Interiors of fractured orthopyroxene that hosts carbonate are homogeneous to within $\pm 1\%$. (4) Secondary SiO_2 has a $\delta^{18}\text{O}$ of 20.4‰. These data are inconsistent with mutual O isotope equilibrium among carbonate and silicate minerals and indicate either fine scale mineral-mineral equilibrium at a range of temperatures $\leq 300^\circ\text{C}$ or a failure to attain mineral-mineral equilibrium. Mineralogical evidence for disequilibrium supports the latter interpretation. Our $\delta^{18}\text{O}$ values for carbonates have been confirmed by two studies [3], and extended to compositions of carbonate not found in our sample.

Ranges in $\delta^{18}\text{O}$ among carbonates in ALH 84001 and other SNC meteorites have in the past been interpreted as temperature constraints based upon fluid-carbonate equilibrium (likely in any case) and models for the isotopic composition of martian volatiles [e.g., 4]. Constraints using our data and such models are: (1) variations in temperature during precipitation from a salt-free, juvenile, H_2O - CO_2 fluid—temperature range must be 0° – 175°C . (2) Variations in the temperature of precipitation from an aqueous fluid of constant salinity and (unknown) $\delta^{18}\text{O}$ —temperatures must have ranged up to at least 50°C . If salinity and temperature covaried, these limits are relaxed and the maximum temperature could have been somewhat lower. (3) Changes in chemical composition of the fluid (e.g., $\text{CO}_2/\text{H}_2\text{O}$ ratio) at constant temperature—
temperature less than

300°C . (4) Precipitation from two or more fluids of different $\delta^{18}\text{O}$ —no temperature limits. No one of these models can be preferred using existing data. Consideration of recent data by Gilmore et al. and Leshin et al. in terms of these models result in relatively minor changes from these limits. Other models appear generally plausible but are contradicted by the existing data (e.g., variation in $\delta^{18}\text{O}$ due to Rayleigh distillation from CO_2 -rich fluid, suggested by [3]) violates the covariation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ determined for ALH 84001 carbonates by partial dissolution experiments [5] and violates the expected relationship between the bulk isotopic composition of carbonate and the range determined by ion probe.

We conclude that no rigorous temperature constraint can be made using existing data, and that the best estimate derives from comparison with terrestrial analogies for the processes that led to the observed metastable mineralogy, isotopic variability and oscillatory chemical zoning. The best terrestrial analogies of which we are aware are: (1) diagenetic siderites, (2) carbonate weathering products of ultramafic rocks, and (3) carbonates precipitated from aqueous fluids in subgreenschist facies crustal rocks. The temperature limits indicated by these analogies are uncertain, but imply a maximum of $\sim 300^\circ\text{C}$ and typically occur only at near-surface temperatures. This interpretation is consistent with (but does not indicate) biological activity during carbonate precipitation. Of more general significance, this interpretation indicates that carbonates in ALH 84001 are an example of CO_2 dissolved in aqueous fluids being sequestered in carbonate minerals in the martian crust. While the extent of this process on Mars is unknown, this geochemical cycle is among the most important interactions between the crust and atmosphere on Earth.

References: [1] McKay et al. (1996). [2] Valley et al. (1997) *Science*. [3] Gilmore et al.; Leshin et al. (1997) *LPS XXVIII*, verbal communication. [4] Clayton and Mayeda (1988). [5] Romanek et al. (1994).